THE PREPARATION OF A SUPERALLOY
WITH CONTROLLED POROSITY

BRUCE EDMOND GLENDINNING

1953

Library
U. S. Naval Postgraduate School
Monterey, California

113-94

THE PREPARATION OF A
SUPERALLOY WITH CONTROLLED
POROSITY

D. E. Glendinning

Library
U. S. Naval Postgraduate School
Monterey, California

THE PREPARATION OF A SUPERALLOY WITH CONTROLLED POROSITY

by

Bruce Edmond Glendinning
Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of
MASTER OF SCIENCE
IN
MECHANICAL ENGINEERING

United States Naval Postgraduate School
Monterey, California
1953

G458

This work is accepted as fulfilling
the thesis requirements for the degree of

MASTER OF SCIENCE

IN

MECHANICAL ENGINEERING

from the

United States Naval Postgraduate School

PREFACE

The work described in this paper was accomplished during the period January to May 1953 at the U. S. Naval Postgraduate School, Monterey, California as an experimental thesis partially fulfilling the requirements for the degree of Master of Science in Mechanical Engineering.

The author is indebted to the several members of the Metallurgy Department for their assistance and interest in the project and especially to Professor Frederick L. Coonan for his guidance throughout the course of the investigation. He also wishes to acknowledge the careful and painstaking work accomplished by Mr. Joseph Octavek in repairing the damage to the experimental die used in this work.

TABLE OF CONTENTS

		Page
Preface		ii
Table of Contents		iii
List of Illustrations		iv
Summary		1
Chapter I	Introduction	2
Chapter II	Materials	5
Chapter III	Mixing of Powders	8
Chapter IV	Die Design	12
Chapter V	Pressing Operations	16
Chapter VI	Sintering Atmosphere and Purification System	22
Chapter VII	The Furnace and Sintering Operations	24
Chapter VIII	Volumetric Changes During Sintering	27
Chapter IX	Metallographic Examination of Specimens	30
Chapter X	Density and Porosity Measurements	31
Chapter XI	Hardness Measurements	34
Chapter XII	Machining of Porous Specimens	35
Chapter XIII	Permeability Measurements	36
Chapter XIV	Conclusions	36
Chapter XV	Recommendations	37
Bibliography		40
Appendix		42

LIST OF ILLUSTRATIONS

1. High Pressure Die for Compressing Metal Powder
2. High Pressure Die and Parts
3. Method of Filling Die With Powder
4. Die Assembly Under Load In Testing Machine
5. Specimens After Pressing, Sintering, and Rough Grinding
6. Helium Purification System
7. General View - Furnace and Purification System
8. General View - Furnace and Purification System
9. Furnace Arrangement
10. X-40 Compacted At 100,000 psi and Sintered For Four Hours at 2100°F. Etched With Chromic Acid and Alkaline Potassium Permanganate
11. Porosity of Porous X-40 Specimens Prepared With (A) 3.85%, (B) 7.42%, (C) 10.79% and (D) 13.60% Ammonium Bicarbonate
12. Porosity Variation For Different Conditions
13. Shrinkage Variation For Different Conditions
14. Flow Rate vs Pressure Difference
15. Permeability Coefficient vs Porosity.

SUMMARY

The objective of this work was to manufacture by powder metallurgy techniques a porous superalloy which could be used for sweat cooling applications.

Elemental powders with the composition of X-40 were pressed at high pressures and sintered at high temperatures to form a basic material. By use of ammonium bicarbonate as a pore producing agent the porosity was controlled uniformly.

As a result of this investigation it was found that:

(1) The optimum compacting pressure was 100,000 psi.

(2) The optimum sintering temperature was 2100°F.

(3) The specimens produced were soft but had high wear resistance.

(4) The maximum relative density achieved was 76%.

(5) Controlled variations in porosity were achieved between 24 and 52%.

(6) The permeability coefficient varied linearly with porosity.

(7) The use of a salt impregnation technique to preserve metal porosity during machining operations was effective in preserving pore structure but the salt could not be readily removed.

CHAPTER I

INTRODUCTION

The use of higher and higher temperatures in new forms of power plants has imposed the most extreme requirements on the engineering materials used in their construction. Two approaches have been used to this problem. The first entails the production of better materials which will maintain their properties and performance characteristics while actually heated to these higher temperatures. The second approach envisions the use of a coolant to reduce the temperature to which the metal parts are actually subjected.

The orthodox application of the latter approach is common engineering practice but the application of sweat or transpiration cooling is comparatively recent. In this type of cooling a porous metal is employed and a coolant is forced through the pores. The cooling fluid may be either a liquid or a gas and the manner in which it is used will determine the cooling characteristics obtained. The cooling action consists of (1) a mechanical absorption of heat from the metal while passing through the pores, (2) the formation of a cool layer of insulating vapor on the flame side of the metal, and (3) in the case of a liquid coolant, the cooling effect achieved by evaporation on the exposed wall.

The dramatic effects of sweat cooling are best expressed in terms of the results achieved by investigators in this field. Hoffman and Gillette[5], with an estimated flame temperature of 3500°F, report a maximum wall temperature of 197°F using .1 $cc/sec\text{-}in^2$ of water as the coolant flow. By the use of air cooling for a gas turbine blade Eckert and Esgar[4] show a blade temperature 650°F below that of the gas stream.

The method of preparation of the porous metals consists of adding a gas producing agent to a metal powder, compressing the mixture under high pressure and then sintering to achieve the formation of continuous metal phase interlaced with interconnecting pores. From a design point of view the use of a porous metal requires close control of the permeability in order to assure the correct flow rate of the coolant under specified conditions of pressure drop. In practice the required flow rate would be calculated from heat transfer data and the pressure drop established from other design considerations. The permeability required of the porous metal would then be calculated and a porous metal specified on the basis of the amount of gas producing agent used.

Many materials have been fabricated for this application, probably the most successful being stainless steel compacts with ammonium bicarbonate as the porosity inducing agent. Subsequent research however, has shown that porous stainless steel, when subjected to the severe temperature conditions of rocket

motors, exhibits a tendency to crack from thermal stresses.

In this investigation an attempt has been made to prepare a porous metal suitable for transpiration cooling from a cobalt base alloy of the high temperature superalloy group. The alloy chosen was X-40 (Haynes Stellite 31) in order to obtain maximum mechanical properties at elevated temperatures in combination with the corrosion and wear resistance necessary to resist the flow of hot combustion gases as well as better resistance to thermal cracking. The use of this alloy in sweat cooled applications should permit the use of greatly increased flame and gas temperatures without the loss of material strength. It is conceivable that wall temperatures on the order of 16-1800°F may be utilized thereby permitting gas temperatures several hundred degrees higher. Such an alloy could possibly be adapted for use in proposed nuclear power plants for aircraft propulsion where the most extreme temperature conditions are likely to be encountered.

CHAPTER II

MATERIALS

The powders used in the production of the porous specimens were obtained from various sources as tabulated in Table I.

TABLE I

POWDERED METALS - SOURCES AND DESCRIPTION

METAL	SUPPLIER	MESH SIZE	PURITY
Cobalt	African Metals Corp. 25 Broadway New York, N. Y.	-300	97.98%
Tungsten	Fansteel Metallurgical Corp. 2200 Sheridan Road North Chicago, Ill.	-325	99.9%
Nickel	Metals Disintegrating Co. Elizabeth, N. J.	-100 50% -325 (MD102)*	99.25%
Chromium	Electro Metallurgical Division Union Carbide and Carbon Corp. 30 E. 42nd St. New York, N. Y.	-20 reduced by milling to -140	97.95%

* manufacturer's designation

In selecting the proper particle size for use in compressing briquettes Goetzel[5] advises the use of fine powders and the finest powders commercially available were secured for this work. The exception to this was the chromium powder which was available only as a mixed powder passing through a twenty mesh screen.

The chromium powder as received was too coarse to be adapted for this type of work. The first step was to process the entire batch through a series of U. S. standard screens arranged in the following cascade of mesh sizes -- 70, 140, and 270. The powders segregated approximately as follows:

50%	+70	
40%	-70	+140
9%	-140	+270
1%	-270	

where - indicates passing through and
+ indicates remaining on the screen.

It was considered impractical to attempt reduction of sufficient powder to permit use of -270 mesh chromium and therefore -140 +270 powder was used throughout the investigation and is designated herein as -140 mesh chromium. Additional powder of -140 mesh was obtained by grinding the coarser powders in two mechanically driven mortars and pestles made of mullite. With a grinding period of two hours a yield of about 20% of the desired powder size could be obtained. Sufficient powder to complete the investigation was obtained in this manner but considering the very small quantity of material handled by these machines (approximately one teaspoon each two hours), it would not appear feasible to attempt an

investigation requiring substantially larger amounts of chromium powder. It had been planned to attempt reduction by use of a hammer mill but the lack of a suitable screen precluded its use in time to prepare powder for this investigation.

In order to achieve a minimum porosity for the basic metal it was necessary to have a gradation in particle size. This was only partly attained in that the cobalt powder forming nearly 60% of the mix was all of one mesh size. The use, however, of chromium powder of a larger mesh (-140) and a nickel powder of graded composition serves to partially compensate for this shortcoming.

CHAPTER III

MIXING OF POWDERS

For this investigation a standard mixture of the four basic elements of X-40 was adopted and used throughout the investigation. The composition of this mixture by weight percentage was as follows:

COBALT	57.5%
CHROMIUM	25.0%
NICKEL	10.0%
TUNGSTEN	7.5%

No attempt was made to include the 1% of iron nor the .5% of carbon in the standard composition. It is felt that it would have been desirable to include the carbon since the hardness of the material depends to a great degree on the formation of carbides.

To the above mixture was added a standard 1% of lithium stearate (Li C_{18} H_{35} O_2) in the form of Lithnolite* to act as a lubricant for the powder during the pressing operation. The addition of this small amount of internal lubrication had a definite salutary effect on the pressing operation as compared with attempts to press unlubricated powder as judged by the increased compression ratio, lack of striations or laminar bands and the complete elimination of the grinding and crushing noises which were markedly apparent with unlubricated

---

* Product of Foote Mfg. Co., Phila, Pa.

powder. The use of some form of internal lubricant is considered an absolute necessity in this type of high pressure compaction in order to achieve uniform density, to preserve the die and plungers and to insure a smooth finish on the compacts. It should be noted, however, that in this case the percentage chosen may not be the optimum nor the minimum requirement for satisfactory compaction but was used throughout to obtain uniformity of the mix and elimination thereby of one of the many variables in the problem.

The use of lithium stearate was predicated on the information of Goetzel[5] on the use of lithium vapors as a reducing and drying agent for water vapor and oxygen originating within the compacts. This was considered as a very valuable and important function in view of the oxides and water vapor probably present within the compact. The use of calcium stearate as a lubricant in the very first run attempted appeared to produce a sintered metal of the same quality as those produced with the lithium salt. No quantitative evidence is available to evaluate the relative value of these two lubricants.

Using the standard mix referred to above, the powders were mixed in an Abbe ball mill for a period of twenty-four hours. For the first few runs only sufficient powder was mixed to permit pressing operations on a daily basis for each individual furnace heat. As the sintering schedule became

stabilized and as the ground chromium powder became available, larger batches of the X-40 mix were prepared to use as stock for further addition of the ammonium bicarbonate in various percentages. The mixing of the powder blend caused no undue difficulty.

The addition of ammonium bicarbonate as the gas producing agent was accomplished by keeping the powder refrigerated with dry ice during the mixing operation to prevent dissociation of the bicarbonate. This mixing operation was carried out with the Abbe ball mill but with the 10" diameter mullite jar modified by the insertion of a concentric steel cylinder, 4" in diameter, which held the balls and powder to be mixed while the annular space between the walls was filled with dry ice. A wooden cover with suitable holes for the escape of the carbon dioxide completed the assembly.

Originally it was planned to mix the ammonium bicarbonate with the basic X-40 for twenty-four hours to insure adequate blending and pulverization of the bicarbonate powder. Trial runs demonstrated that the amount of dry ice required was large, with ten pounds of the refrigerant lasting only two hours. With this restriction the blending time was limited to two hours. The resultant mix showed no trace of ammonium bicarbonate and the porosity produced was reasonably uniform.

The ammonium bicarbonate used was sifted through a 70 mesh screen and was then added as a percentage of the amount

of metal powder being used. All expressions of bicarbonate content in this paper, however, are expressed as a percentage of the total weight of the mix.

After mixing and while pressing the powder mix containing ammonium bicarbonate was stored under mechanical refrigeration at -40°F to prevent dissociation until the powder was actually in its final pressed form. No appreciable dissociation could be detected under these conditions, but it was noticed that a slight amount of water vapor was condensed on the surface of the powder.

After pressing, no further attempt was made to prevent dissociation and the compacts were allowed to reach room temperature until placed in the furnace for sintering.

CHAPTER IV

DIE DESIGN

The pressing of specimens was accomplished in a die designed especially for this project. In order to produce results conveniently with the equipment available the size of the specimen was limited to 7/8" in diameter. Thus by using a Universal Testing Machine in compression with a maximum load of 60,000 pounds, a pressure of 100,000 pounds per square inch on the faces of the specimen could be produced since the face area was .6 square inches. This arbitrary size imposed on the specimens severely limited the amount of testing which could be accomplished on the finished products since their small size precluded the manufacture of tensile specimens in any of the standard configurations. The cylindrical shape was established as the simplest and most convenient configuration for the die manufacture and also as being the most adaptable to further testing of permeability by gas flow through the specimen.

In order to achieve the smallest variation in compact density it is necessary to utilize a press with a double acting plunger movement so that compressive motion is applied to the powder from opposite directions. Unless this double action is applied, the variation in density along the axis of pressing will vary radically, decreasing as the distance

from the compressing face increases. The application of the principal of the floating die eliminates the need for two moving plungers in that the die is supported by springs, and hence is free to move when acted upon by the wall friction of the powders being compacted. The movement of the die permits relative motion by the second plunger and hence compression from the second direction. This is illustrated in Figure 1. Imagine that a mass of powder to be compressed is contained in the die body between the faces of the plungers while a uniaxial compressive force is applied on the upper plunger. The first action of the plunger will be to compress the upper layer of the powder into an archlike bridge bearing against the walls of the die cavity. This vertical force transmitted to the die body causes it to move downward and compress the rubber springs. Thus, in effect, the lower plunger moves up an equivalent distance relative to the powder mass and compression is attained from both top and bottom of the compact. In operation interparticle friction within the compact balances the rate of compression of the two plungers so that movement, and hence densification, progresses equally from both ends.

In the design of this die no information was available on the frictional effect to be expected when using a powder mix of the K-40 composition. The figure used for design, therefore, was based on the data of Unckel as reported by Goetzel[5] for iron powders lubricated with graphite. The

figures given by Unckel indicate that .4 of the compaction force is translated to the die wall for a 100 g. iron compact and that figure was used in this work. It should be noted that the percentage of the load translated to the die wall is a function of the lateral surface of the die cavity exposed to the powder or more simply a function of the height of the powder fill. The springs for this die were designed for a load of .4 x 60,000 or 24,000 pounds, but the springs used were of a "softer" rubber than is indicated. It is evident that if the rubber is over-compressed the force is immediately translated to the lower plunger and thereby to the under side of the powder compact, thus relieving the overcompression of the springs. The original calculations were made for an estimated compression ratio of 3 and a finished compact height of .775" which required a compression of the rubber springs equal to 1/2 the difference between the height of the powder fill and the height of the pressed compact, equal in this case to .775". The area, thickness, and hardness of the rubber springs required was calculated on the basis of the combined data of Wall[13] and Valance and Doughtie[12], and in accordance with the following formula:

$$y = \frac{Kc}{A^{1/2}E}\left(E_{55}\, y_{55}\right)$$

where y - deformation, in.

A - loaded area, sq.in.

E - modulus of elasticity, psi

K_c - form factor corresponding to the ratio of the loaded circular areas to the total surface area

E_{55} - modulus of elasticity of 55 durometer rubber, psi

y_{55} - deflection of a 1 in. cube of 55 durometer rubber, in.

The hardness required to meet the above specified conditions was durometer number 85 but the actual springs used were fabricated of three one-inch layers of a somewhat softer rubber which was available for use. Concurrently the maximum height of the compact was reduced to .5 inch and the length of the lower plunger (C) was increased by .45".

The die cylinder was designed on the basis of Lamé's formula[8] for thick-wall cylinders subjected to high internal pressure. In its most convenient form for this application the formula is

$$R = r\sqrt{\frac{S+P}{S-P}}$$

where R - outer radius of cylinder in inches

S - maximum allowable fiber stress per square inch (taken as 40,000 psi)

r - inner radius of cylinder in inches

P - pressure within the cylinder in pounds per square inch.

The maximum allowable fiber stress was taken as 40,000 psi, the inner radius had already been fixed at 7/16" and the maximum pressure at which the compacts were to be pressed was 100,000 psi. As pointed out by Goetzel[5], however, the lateral pressure exerted on the walls of the die is not the same as the pressure on the faces of the plungers when compacting metal powders, since these powders do not act as a hydrostatic medium. The value of P, therefore, was calculated by multiplying the value of the compacting pressure by Poisson's ratio, giving in this case a wall pressure of 30,000 psi. The value of R as thus calculated is 1.75" (D = 3.50") and the diameter was arbitrarily increased to 4.00" in order to achieve greater stability of the die body and to give a somewhat greater factor of safety.

The clearances between plungers and die were based on the important consideration that an exit must be provided for any entrapped air during the compression stroke which would otherwise cause laminations in the compact. If, however, the clearance is too large the microscopic particles of the powder will find their way between the moving surfaces and cause galling, scratching and even weld themselves to the die parts. The clearance chosen, therefore, was based on the engineering "snug fit" and approximates .0005" based on the diameter of the plunger. (See figure 1 for actual tolerances). Since in this case compression was to be slow

hydraulic pressing it was felt that the danger from entrapped air was minimized.

The die cavity in which the compacts were pressed was designed with a 6' draft or taper as an aid in ejecting the pressed compacts. This taper was produced in the finished compacts but was of no importance.

Goetzel[5] recommends a hardness of Rockwell C 45 for the die body and Rockwell C 40 for the plungers for experimental dies of this type but in this case the hardness for both die and plungers was specified as C50 due to the extreme hardness and abrasive nature of the powders.

The die and plungers as described above where fabricated under contract at the United States Naval Shipyard, San Francisco, Calif. The material used was a hard tungsten tool steel.

CHAPTER V

PRESSING OPERATIONS

On receipt of the dies and plungers work was commenced using iron powder in order to measure the actual compression of the rubber springs and the effectiveness of the floating die principle outlined above. Two specimens (30 gram fill) were pressed satisfactorily at 60,000 psi but after the third pressing great difficulty was experienced in ejecting the compact. It was found that the upper plunger was tightly jammed in the die body. Attempts to withdraw the plunger by pushing on the bottom face were unsuccessful. A total movement of 3/4" was achieved before these efforts were discontinued since a force of 40,000 pounds produced no further movement. The projecting part of the upper plunger was then sawed off and retained for further use while the plunger remaining in the die was drilled, bored and ground out in careful sequence. The die walls had been scored and galled by this casualty but by careful grinding the die was restored to usefulness. Part of the cavity in the tapered section remained undamaged and subsequent pressing operations were confined to this undamaged area. As a result of this damage the height of the finished compacts was limited to .3" and after extensive operation increased to .4".

The causes of this damage were:

(1) Failure to lubricate the die parts or the powder.

(2) Failure to clean the die walls of powder before inserting the upper plunger.

(3) The use of iron powder with the steel die so that the similarity of the two metals had a greater tendency to promote cold welding.

In order to reduce the lateral surface exposed to the welding action of the powder, three sections were cut from the upper plunger, each 3/4" in length, with the faces ground at right angles to the axis. One of these segments was used as a dummy compression piston throughout the further work. An additional plunger, considerably undersized, was fabricated from mild steel to transmit the applied force to the dummy piston. This member proved satisfactory at 50,000 psi but for the pressings at the higher pressures of 80 and 100,000 psi another plunger was fabricated of high speed tool steel. This plunger was preheated for one hour at 1000°F and then quenched from 2250°F in oil. A one hour tempering at 1100°F produced a final hardness of Rockwell C57. The several parts are shown disassembled in Figure 2.

To prevent a recurrence of the casualty described, the following procedure was carefully followed in subsequent pressing operations:

(1) All parts were kept scrupulously clean. After each pressing the parts were wiped clean with a cloth.

(2) Both plungers were carefully lubricated by hand using a high grade pressure grease (Lubriplate-ball bearing grade).

(3) An internal lubricant was included in the powder mix as discussed under Mixing of Powder.

(4) The die cavity was filled by means of a centrally positioned glass funnel as shown in figure 3. This prevented the deposition of large amounts of powder on the die walls.

(5) After filling the die cavity the powder was levelled and the walls were wiped clean with a cotton swab and inspected before the dummy plunger was inserted.

(6) The die parts were demagnetized.

The above procedure while laborious was considered to be essential to further operations with the die. By following this procedure a total of ninety-four pressings were made and it is estimated that with careful use the die would produce five times that number.

The time consumed in these operations was probably disproportionate to the results achieved, since the first specimens required an average of thirty minutes each. With increasing experience this was reduced to less than fifteen minutes per pressing.

The pressing procedure was to increase the load at a rate of 1000 pounds per second to the designated load which

was held for five seconds. The die assembly is shown under compression in Figure 4. The load was then reduced at an approximate rate of 2000 pounds per second. After unloading, the lower plunger was removed and the load was again applied to eject the pressed compact. The force required for ejection varied between 400 and 600 pounds but was observed to be constant for any type of compact.

It was found necessary to catch the ejected specimen on a small wad of cotton to prevent the formation of cracks which made the specimen worthless.

The compacts produced at pressures in the range 60 - 100,000 psi had excellent green strength and were characterized by a bright shiny finish with sharp edges. Under normal handling these sharp edges were preserved throughout the sintering operation. The green compact is illustrated in Figure 5. The particular specimen illustrated had been subjected to handling which caused the worn edges. The pressures of 80 and 100,000 psi produced compacts with a firmer, shinier and more solid appearance.

The compression ratios achieved with this powder are tabulated in Table II.

TABLE II

Compacting Pressure (psi)	Compression Ratio
60,000	1.655
80,000	1.735
100,000	1.785

CHAPTER VI

SINTERING ATMOSPHERE AND PURIFICATION SYSTEM

Helium was chosen as the atmosphere used during sintering primarily because of its inert nature. Several incidents where helium escaped into the operating furnaces during the course of the investigation confirmed the soundness of this selection. Also as a result of work by other investigators the use of helium instead of hydrogen has been demonstrated to increase the tensile strength of powder metallurgy products by as much as twenty per cent.

The purity of the atmosphere is essential for the achievement of proper sintering of the alloy and all traces of oxygen and water vapor were removed.

The starting point of the helium train was standard U.S. Navy Grade A helium. This gas is approximately 100% pure and is entirely free of oil vapor. In order to remove any impurities the gas purification train as shown in Figure 6 was used. Briefly this consisted of a tube furnace maintained at 1000°F containing copper turnings through which the gas was passed in order to absorb oxygen. This was followed by two drying towers, containing potassium hydroxide and calcium chloride respectively, and a mechanical filtering tower containing loose cotton to retain any solid particles carried over from the two preceding chemical towers.

The gas was then passed through a vapor trap consisting of a coil of glass tubing submerged in liquid nitrogen. All liquid nitrogen used in this work was furnished through the courtesy of the Microwave Laboratory, Stanford University.

The gas system was operated at an inlet pressure of 2 psi gauge against a back pressure of about 1/2 inch of water at a flow rate sufficient to maintain a steady stream of bubbles in the water to which the gas was discharged. On commencing a run a higher flow rate was maintained for about one hour in order to clear the system of impurities and as an aid in clearing the furnace tube or smoke and gases generated in the compacts. Some trouble was experienced with clogging of the exhaust tube with a yellow greasy substance expecially during those runs with high ammonium bicarbonate content. This problem arose principally because of the small inner diameter (1/16") of the glass tubing used but was quickly overcome by passing a wire through the tubing to clear the stoppage and restore flow.

It was noted that at extremely high flow rates the helium leaving the liquid nitrogen cooling coil would freeze the rubber hose for distances up to three feet or to the point where the gas actually entered the furnace. This phenomenon occurred only under unusual conditions of high flow rates and was not normally of any consequence.

CHAPTER VII

THE FURNACE AND SINTERING OPERATIONS

The furnace used in this investigation was a Burrell High Temperature tube furnace (Model CF81-9) and is illustrated in Figures 7, 8, and 9. This furnace operated smoothly throughout the course of the experimentation except for the tube trouble discussed below. Control of furnace temperature was achieved by means of a Wheelco wall mounted controller operating from a Platinum-Platinum 13% Rhodium thermocouple which was encased in a 5/8" sillimanite protecting tube inserted axially in the furnace tube. The original furnace tube was a 1 7/8" O.D. type 304 stainless steel welded tube.

In order to achieve proper sintering of the X-40 mix it was estimated that the sintering temperature should be in the range 2000-2400°F. Runs were commenced at a nominal 2200°F with the intention of establishing an optimum temperature. Run 1 was apparently successful and Run 2 was conducted at the same temperature, but a chromium powder of -270 mesh was substituted for the -140 mesh used in Run 1. These specimens all showed a uniform expansion rather than the expected contraction inherent in the sintering process. For Run 3 the temperature was increased to 2400°F and on this run great difficulty was encountered in maintaining satisfactory helium

flow through the furnace. After the furnace had cooled it was discovered that the stainless steel tube had been completely burned through and separated into two parts.

In order to continue the work a sillimanite tube with a 1" inner diameter was substituted and this type of tube was used throughout the remainder of the investigation. This tube required the sealing of the 5/8" thermocouple protecting with refractory cement which prevented routine disassembly.

After Run 4 the specimens were found to be completely melted and both furnace and thermocouple tubes were fractured in attempting disassembly. The furnace tube was replaced and the thermocouple tube repaired using an undersize closed quartz tube and refractory cement. The temperature control system was then calibrated and the controller was found to be 200°F in error. Subsequent furnace operations were controlled by potentiometer readings using the controller only to maintain measured temperature. Temperatures for subsequent runs varied ±30°F due to the action of the controller.

On the basis of density measurements (q.v.) a sintering temperature of 2100°F was selected and used for all runs subsequent to Run 5B. This was done in order to obtain gradations in porosity in the time available.

The operating procedure for the furnace consisted of starting at the lowest possible voltage and amperage rating

and increasing these values slowly but steadily. In the temperature range above 1000°F temperature increase was limited to an average rate of 5°F per minute in order to prevent thermal cracking. No abnormalities were observed in the specimens which could be traced to excessive heating rates except as mentioned in the section on volumetric changes.

Sintering temperature was maintained on all runs for four hours. This was an arbitrary figure and in view of the results achieved is considered to have been too short by a substantial amount.

On completion of the sintering period the specimens were furnace cooled to room temperature. Due to the small size of the furnace this cooling rate was about 10°F per minute. During cooling the helium flow was maintained for 45 minutes or until the temperature reached 1000°F. The helium flow was then discontinued and the flow system tightly closed to maintain the atmosphere during subsequent cooling.

CHAPTER VIII

VOLUMETRIC CHANGES DURING SINTERING

Duwez[3], on the basis of dilatometer expansion-contraction curves, shows the interrelation between shrinkage and sintering action to establish the proper temperature for sintering. In this investigation final volumetric shrinkage has been recorded for all runs and is shown in Figure 13 as a function of ammonium bicarbonate content. For specimens containing a pore producing agent the measure of shrinkage does not denote the effectiveness of sintering as it does with the primary metal. The data are presented here as being of interest with respect to the volumetric changes to be expected when producing a porous metal.

Examination of Figure 13 shows that shrinkage decreases with increasing compacting pressures with other factors remaining constant. This is to be expected, for according to Goetzel[5] "The higher the initial density, the smaller is the rate of densification during the sintering treatment, and the smaller also are both the rate of shrinkage and the actual shrinkage". The higher shrinkages observed at greater ammonium bicarbonate percentages are due to the dissociation of this agent and the partial filling of the resultant voids.

After sintering each group it was found that the specimens had adhered to each other. The degree of adhesion varied but was greatest where the specimens had been bound together by

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

wire before placing in the furnace tube. Separation of the specimens was accomplished by blows with a plastic mallet. This serves to corroborate the evidence of Duwez[3] that multiple powder alloys show a rapid expansion during sintering. No data on the thermal expansion characteristics of the X-40 pressed compacts were available other than the thermal expansion coefficient reported by Sweeney [10] for the cast metal. This average value for the range 70 - 1000°F is 8.75 X 10^{-6} in/in°F which would give an overall expansion for a specimen .5" thick of .005". The expansion observed here is believed to have been much larger. It is regretted that no dilatometer expansion data are available for presentation.

It was noted that all primary specimens showed an expansion after sintering along the longitudinal axis and a contraction on the diameter or transverse axis of pressing. This is interpreted as a release of internal stresses which are oriented with respect to the longitudinal axis as a result of the pressing operation. The average results are tabulated in Table III for specimens sintered at 2100°F:

TABLE III

LINEAR DIMENSIONAL CHANGES DURING SINTERING

Compacting Pressure psi	Longitudinal Expansion %	Transverse Contraction %
60,000	.98	1.90
80,000	1.01	1.27
100,000	1.02	1.81

For the compacts pressed at 60,000 psi three specimens were destroyed by the expansion of the gases within the compact. The failures took the form of complete transverse cleavage of the specimens. One failure occurred with a bicarbonate content of 7.4% (Run No. 6) and the other two with a bicarbonate content of 13.8% (Run No. 10). The phenomenon was not observed on any other run and a contributing cause is believed to have been high early heating rates.

CHAPTER IX

METALLOGRAPHIC EXAMINATION OF SPECIMENS

The structure of the primary specimens of X-40 is typical of metals prepared by powder metallurgy techniques. This metal shows a high porosity which is a characteristic inherent in the method of preparation and constitutes a basic difference between metals prepared from metal powders and those obtained by fusion methods. The cause of this so called primary porosity is due in large part to incomplete compaction.

Microscopic examination of the metals shows that it consists of a cobalt rich matrix containing a network of complex carbides and a phase of partially alloyed chromium. Figure 10 illustrates the structure and the degree of alloying of the chromium particles as well as the grain growth which has taken place during sintering.

This micrograph was prepared by light etching with a 2% chromic acid solution followed immediately by etching for seven seconds in alkaline potassium permanganate as outlined by Clark[12].

CHAPTER [illegible]

DENSITY AND POROSITY MEASUREMENTS

The density of a powder metallurgy product constitutes its most important single property as a measure of the effectiveness of the pressing and sintering operation. The apparent density or specific gravity of these specimens was calculated by weight and volume measurements. On the basis of the densities obtained at various temperatures as shown in Table IV a sintering temperature of 2100°F was selected for all subsequent runs. The values represented are an average of the measurements for four specimens:

TABLE IV

DENSITY OF SPECIMENS PRESSED AT [illegible]0,000 PSI

Sintering Temperature	Apparent Specific Gravity (gm/cc)
2000°F	8.18
2100°F	8.28
2200°F	8.14

The range of densities obtained by sintering at 2100°F is shown in Table V where the percentages expressed are based on a specific gravity of cast X-40 of 8.607 gm/cc[2].

TABLE V

VARIATION OF DENSITY WITH COMPACTING PRESSURE

Compacting Pressure psi	Apparent Specific Gravity (gm/cc)	Percent Relative Density
60,000	6.26	73.0
80,000	6.43	74.7
100,000	6.55	76.1

For the sake of comparison the specific gravity of stainless steel compacts produced by Duwez[5] would show relative densities in the range 61-66% for the same compacting pressures. Likewise Goetzel[6] reports that this alloy has been sintered in vacuum "to a quality comparing with that of the cast alloy".

On the basis of the measured apparent densities the porosity of the sintered specimens was calculated by the formula:

$$P = \frac{d - d_a}{d}$$

where P = Porosity (per cent)

d - specific gravity of metal (gm/cc)

d_a - apparent specific gravity (gm/cc)

The results of the porosity determinations are plotted in Figure 12 where each point shown is an average of at least four specimens. The relationship between porosity and the amount of pore producing agent is shown to be essentially linear. It is apparent that higher compacting pressure

measurably increases the effectiveness of the additive in increasing porosity. The range of porosity produced was between 24 and 52%. Photomicrographs of various porosities are shown in Figure 11.

CHAPTER XI

HARDNESS MEASUREMENTS

Selected specimens with their faces ground flat and parallel were tested for hardness by a Brinell Hardness tester using a 500 KG load. The soft character of this sintered material was revealed in the impressions left by the indenter with a small annular area of crushed and yielded material surrounding the hemispherical indentation. Measurements were taken on the inner or primary indentation and are reported in Table VI:

TABLE VI

BRINELL HARDNESS OF X-40 SPECIMENS SINTERED AT 2100°F

Compacting Pressure psi	Brinell Hardness Number (500 KG load)
50,000	52
80,000	68
100,000	77

The extremely low hardness is attributed to: (1) the porous nature of the material which permitted relatively hard particles to move into the voids and thereby a deeper penetration by the indenter and (2) the low carbon content and short sintering time which prevented the formation of sufficient carbides to develop normal hardness.

The normal hardness of X-40 in the cast condition is Rockwell A 64 and the alloy is susceptible to age hardening[1,2].

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

[illegible]

[illegible]

CHAPTER XII

MACHINING OF POROUS SPECIMENS

In order to face the surfaces of the sintered specimens the procedure proposed by Wheeler[14] was used to impregnate the pores with molten sodium chloride. The specimens were immersed in molten salt at 1500°F for twenty minutes and then allowed to cool before grinding the faces. This procedure was effective in maintaining the pore structure during the grinding operation as judged by observation under the stereoscopic microscope. In order to use the metal for a sweat cooling application it is necessary to remove the salt to restore the original permeability of the structure. Attempts to achieve this by boiling in water were unsuccessful. The specimens were boiled for a total of nine hours with hourly changes of the water and at the end of that time were exuding large amounts of crystalline salt. No attempt was made to measure the quantitative effect on the permeability although it was observed that flow rate was considerable below that of untreated specimens. This same ineffectiveness of the leaching operation to remove the sodium chloride is mentioned by Typaldos and Canright[11] who substituted oxalic acid (as recommended by Wheeler) and reported "very encouraging" results.

CHAPTER XIII

PERMEABILITY MEASUREMENTS

In the use of a porous material for a sweat cooling application the designing engineer uses the permeability coefficient to relate the rate of coolant flow and the porosity of the metal. In the typical design problem the engineer will have available the required coolant flow from heat transfer studies and the desired pressure drop from other design considerations. By use of the permeability coefficient the designer can then determine the required porosity and, hence, specify the material to be used on the basis of the amount of pore producing agent which is to be added to the mix.

The permeability coefficient is determined by measuring the flow rate and pressure drop across the porous specimen. In this work four specimens of different porosity were subjected to pressure by compressed air and the resultant flow through the metal measured by means of a gas flow meter. The observed results were then correlated by Darcy's equation, as formulated for laminar gas flow[3]:

$$\frac{Q}{\frac{P_1^2 - P_0^2}{L}} = \alpha \frac{\rho_0}{2 P_0 \mu}$$

where Q - weight rate of flow per unit area (lb/sq in sec)

P_1 - pressure at the entrance side of the porous metal (psi)

P_0 - pressure at the exit side of the porous metal (psi)

L - thickness of the specimen (in)

ρ_0 - weight of the fluid per unit volume at pressure P_0 (lb/cu in)

μ - viscosity of the fluid (lb - sec/sq in)

α - permeability coefficient (sq in)

The data, as observed for the porous X-40 specimens, are plotted in Figure 14 and show that at low flow rates the relation between the pressure-square difference and the flow rate is essentially linear. Due to variation in thickness of the specimens available for study the pressure square difference has been expressed per unit length. Figure 15 expresses the same experimental results but with permeability coefficient as a function of porosity.

CHAPTER XIV

CONCLUSIONS

As a result of the experimental work conducted during this investigation the following conclusions have been formed:

(1) X-40 mixed from the elemental powders can be successfully compacted into briquettes which have good green strength.

(2) The metal compacts can be successfully sintered in a helium atmosphere provided that the helium is absolutely pure and free from oxygen and water vapor.

(3) The method of controlling porosity by the addition of ammonium bicarbonate is a proven technique and is readily adaptable to forming porous X-40.

(4) The sintering time used was too short to permit adequate diffusion and alloying of the chromium powder.

(5) The impregnation of porous metals with molten salt requires a long treatment to restore the original permeability.

(6) More extensive experimentation is required before attempting the use of porous X-40 as an engineering material although the procedure of using a helium atmosphere for sintering appears feasible.

(7) The use of porous X-40 in a sweat or transpiration cooled application should permit the use of increased flame and gas temperatures without the loss of material strength.

CHAPTER XV

RECOMMENDATIONS

On the basis of the results obtained the following recommendations are submitted:

(1) The sintering time used should be increased in order to increase the diffusion of the chromium phase.

(2) Specimens should be prepared in a size and shape which would permit the forming of tensile specimens in one of the standard configurations so that additional mechanical properties of this porous metal may be reported.

(3) Using specimens of the type recommended in (2) dilatometer studies should be conducted in order to fix more exactly the best sintering temperature.

(4) Additional specimens should be prepared in a configuration which would permit the testing and evaluation of the heat transfer properties of the metal while subjected to the flow of a coolant through the pores. Such experiments would permit an evaluation of the metal's resistance to thermal cracking, when subjected to rapid cooling from high temperatures.

BIBLIOGRAPHY

1. Clark, F. H. Metals at High Temperatures. New York, Reinhold Publishing Corporation. 1950

2. Cross, H. C. and W.F. Simmons. Heat-resisting Metals for Gas-turbine Parts. Philadelphia, American Society for Testing Materials. 1946. (Symposium on Materials for Gas Turbines)

3. Duwez, P. and H.L. Martens. The Powder Metallurgy of Porous Metals and Alloys Having a Controlled Porosity (T.P. 2349). New York, American Institute of Mining and Metallurgical Engineers, Inc. April, 1948. (Metals Technology)

4. Eckert, E.R.G. and J.B. Esgar. Survey of Advantages and Problems Associated with Transpiration Cooling and Film Cooling of Gas-turbine Blades. Research Memorandum (NACA RM E50K15). Washington, National Advisory Committee for Aeronautics, February 12, 1951 (Restricted).

5. Goetzel, C.G. Treatise on Powder Metallurgy, Vol. I. New York, Interscience Publishers, Inc. 1949.

6. Goetzel, C.G. Treatise on Powder Metallurgy, Vol. II. New York, Interscience Publishers, Inc. 1950.

7. Hoffman, C.A. and L.S. Gillette, Jr. A Study of Porous Metal Cooling. Pasadena, California Institute of Technology. (Thesis), June, 194[illegible].

8. Machinery's Handbook. New York, Industrial Press, 194[illegible].

9. Metals Handbook, 1948 ed. Cleveland (Ohio), American Society for Metals.

10. Sweeney, W.O. Haynes Alloys for High-temperature Service. New York, Transaction of the American Society of Mechanical Engineers (Vol. 69). August, 1947.

11. Typaldos, Z.A. and R.D. Canright. An Experimental Evaluation of Transpiration Cooling in a Rocket-Motor Chamber, Report No. 1-39. Pasadena, Jet Propulsion Laboratory, California Institute of Technology, June 1[illegible], 1952.

12. Valance A. and Doughtie, V.L. Design of Machine Members. New York, McGraw-Hill, 1943.

13. Wahl, A.M. Mechanical Springs. Cleveland (Ohio), Penton Publishing Co., 1944.

14. Wheeler, H.L. A Method For Machining Porous Metals. Progress Report No. 4-97. Pasadena, Jet Propulsion Laboratory, California Institute of Technology, April 15, 1949.

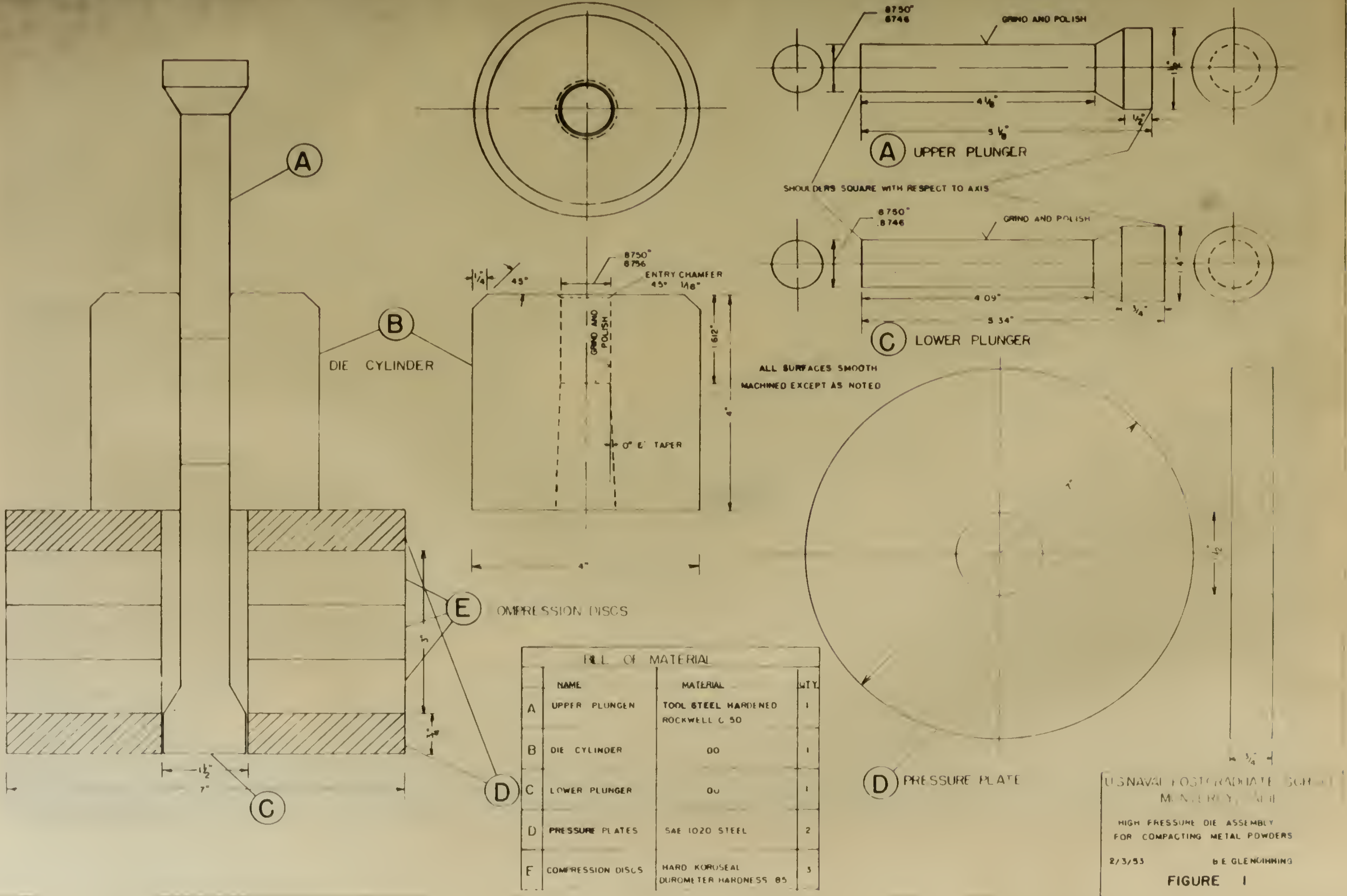
APPENDIX I

SUMMARY OF DATA FOR ALL SPECIMENS*

Run No.	Compacting Pressure psi	Sintering Temperature oF	Density Gm/cc	Porosity %	Shrinkage %	Ammonium Bicarbonate
1	60,000	2400 estimated	6.13	31.[illegible]	2.03	
2	60,000	2400 estimated			expanded	**
3	60,000	2600 estimated	melted			
4	60,000	2600 estimated	melted			
5A	60,000	2000	6.18	28.2	.[illegible]	
5B	60,000	2100	6.28	27.0	3.4[illegible]	
6	60,000	2200	6.14	2[illegible].0	1.25	
7	60,000	2100	5.74	33.[illegible]	[illegible].50	3.[illegible]5
8	60,000	2100	5.08	40.[illegible]	[illegible].[illegible]5	7.42
9	60,000	2100	4.67	45.[illegible]	10.[illegible]5	10.70
10	60,000	2100	4.12	52.2	[illegible].80	13.00
11	60,000	2100	6.43	25.3	1.11	
12	60,000	2100	5.02	41.7	5.[illegible]7	7.42
13	60,000	2100	4.39	4[illegible].[illegible]	5.[illegible]3	10.70
14	100,000	2100	6.55	23.[illegible]	0	
15	100,000	2100	4.93	42.7	2.50	7.42
16	100,000	2100	4.25	51.0	4.70	10.70

* All results are averages of four specimens.

** For Run number 2 chromium powder size was -270 mesh.



BILL OF MATERIAL

	NAME	MATERIAL	QTY.
A	UPPER PLUNGER	TOOL STEEL HARDENED ROCKWELL C 50	1
B	DIE CYLINDER	DO	1
C	LOWER PLUNGER	DO	1
D	PRESSURE PLATES	SAE 1020 STEEL	2
F	COMPRESSION DISCS	HARD KOROSEAL DUROMETER HARDNESS 85	3

U.S. NAVAL POSTGRADUATE SCHOOL
MONTEREY, CALIF.

HIGH PRESSURE DIE ASSEMBLY
FOR COMPACTING METAL POWDERS

2/3/53 B E GLENDINNING

FIGURE 1

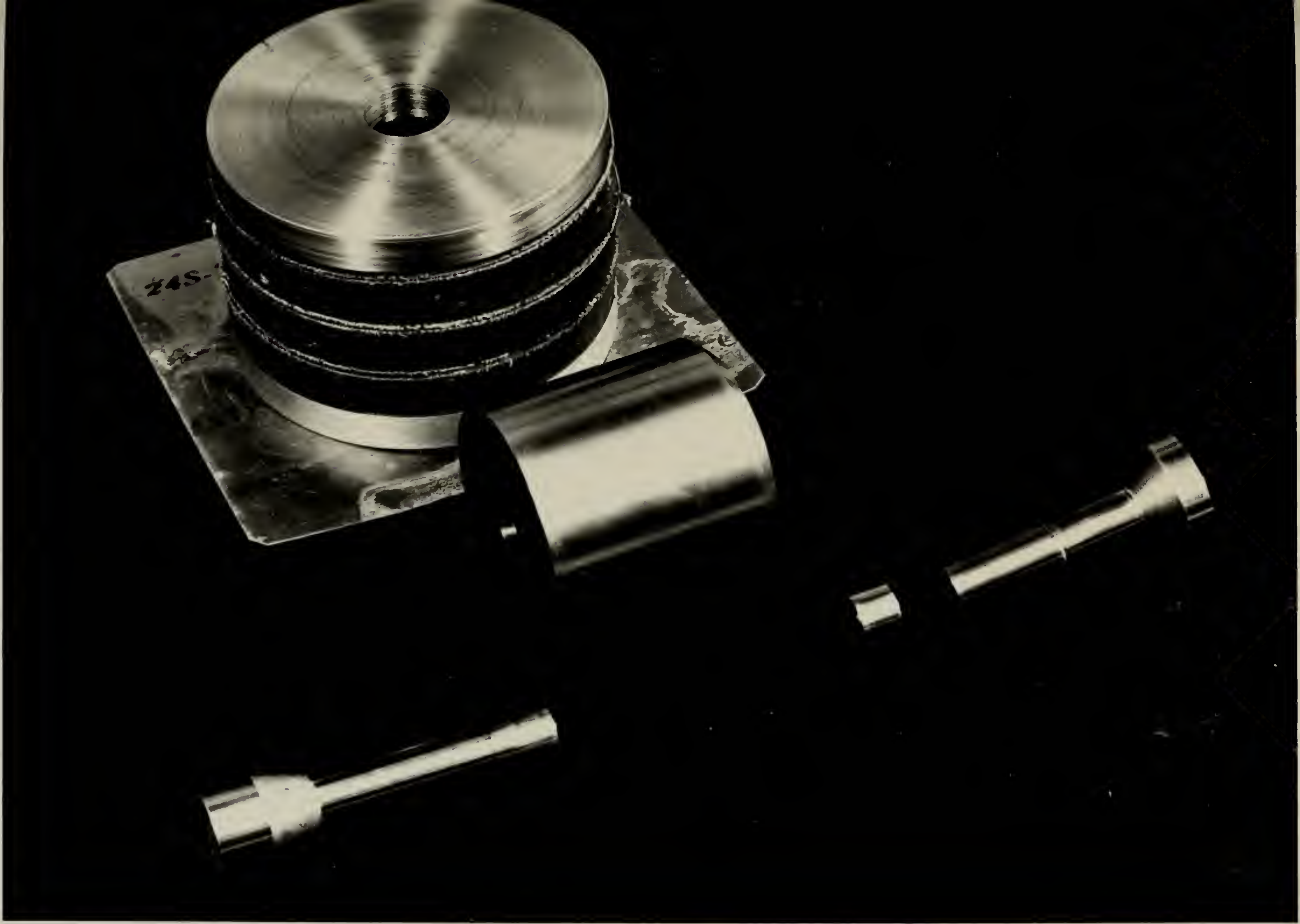


FIGURE 2. High Pressure Die and Parts

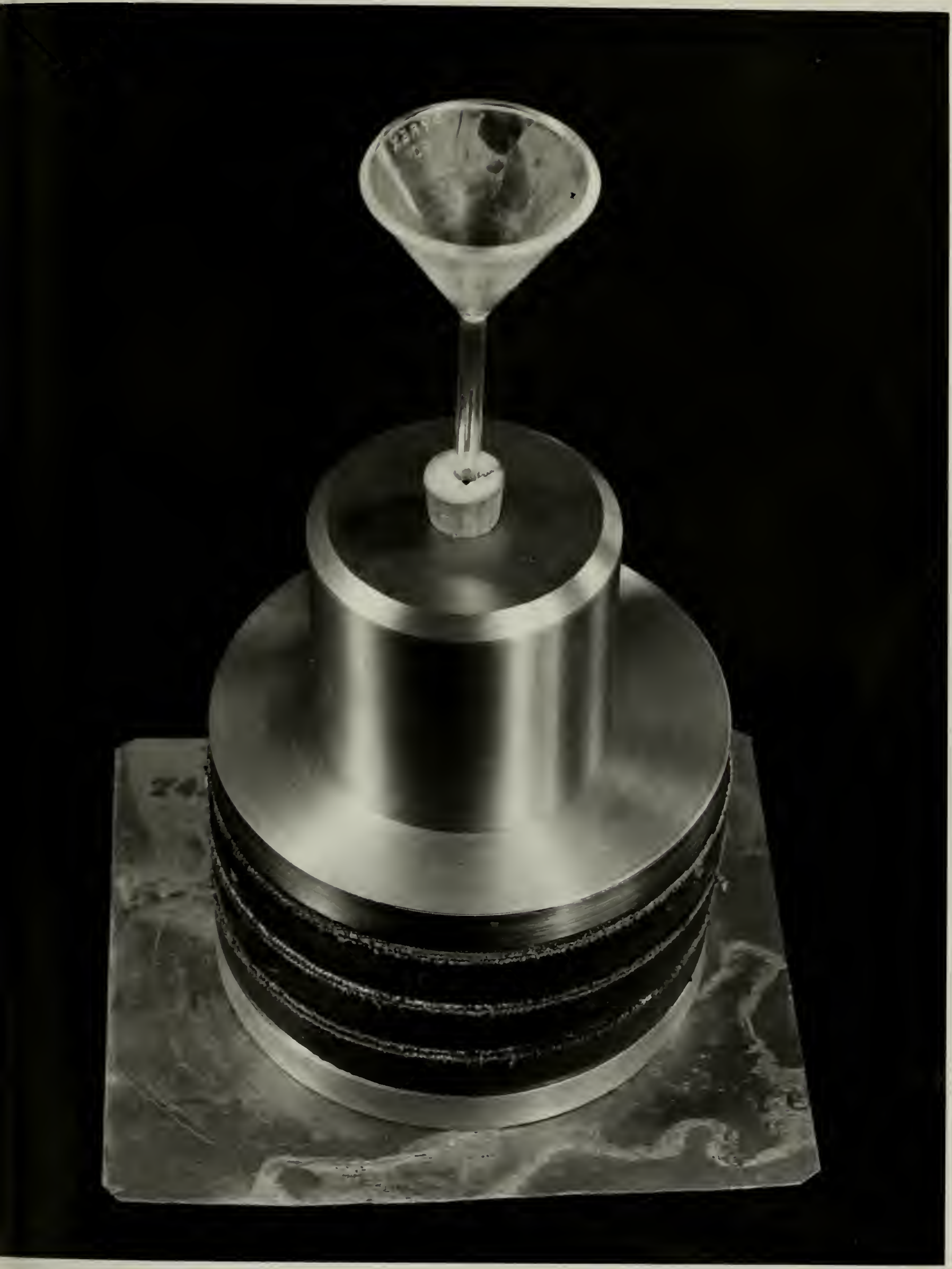


FIGURE 3. Method of Filling Die with Powder

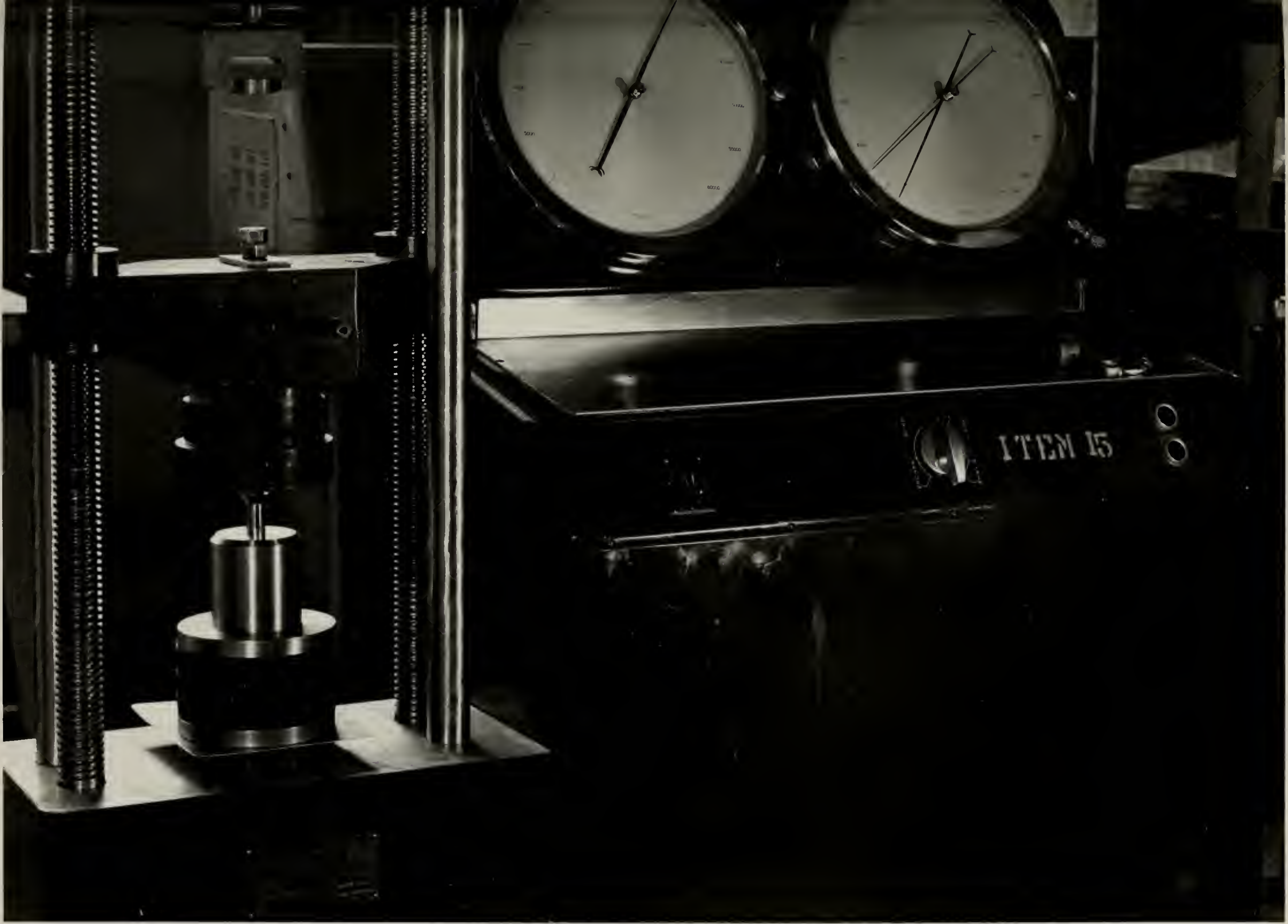


FIGURE 4. Die Assembly Under Load in Testing Machine

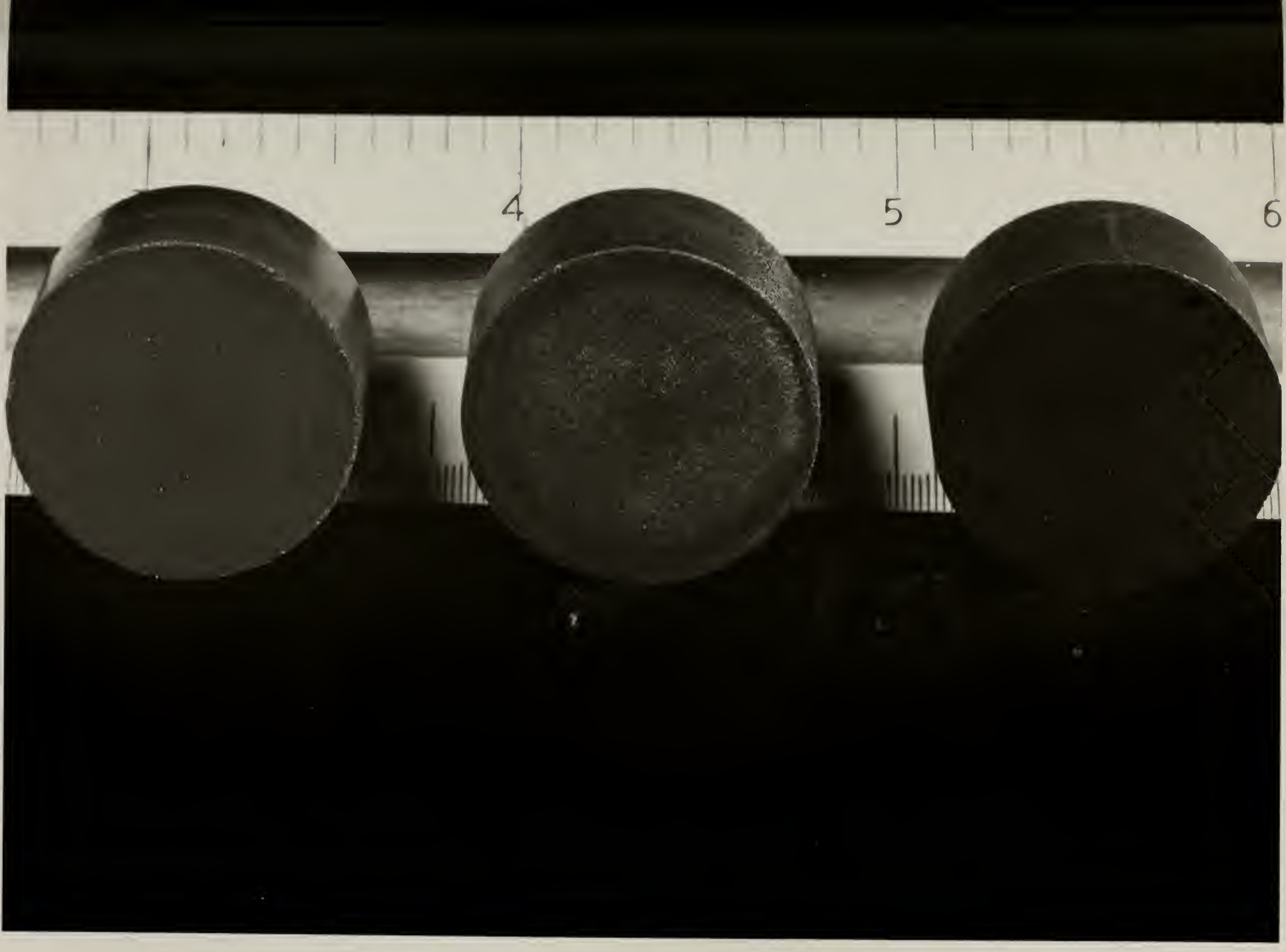


FIGURE 5. Specimens After Pressing (Left), Sintering (Center) and Rough Grinding (Right)

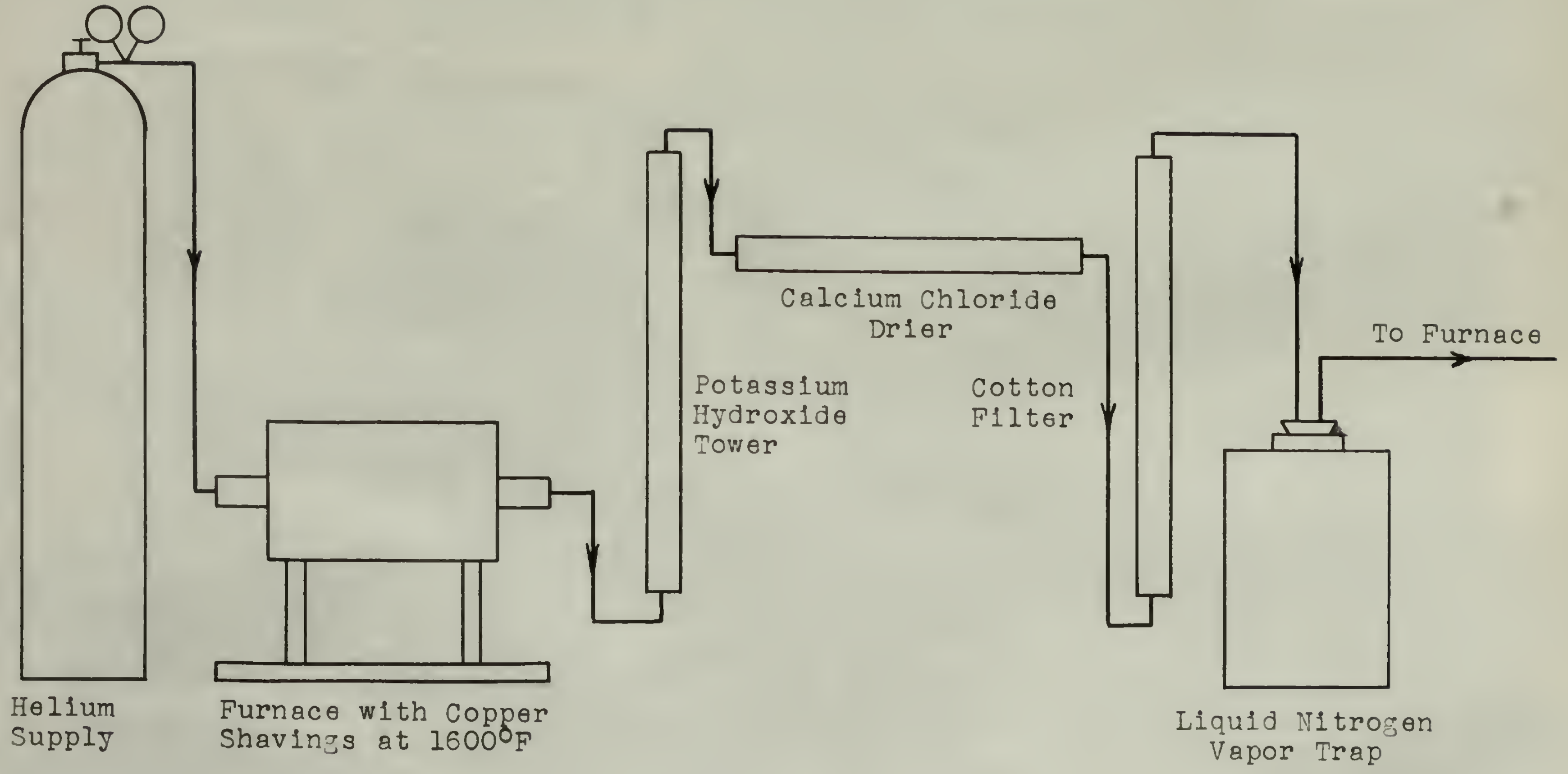


FIGURE 6. Helium Purification System

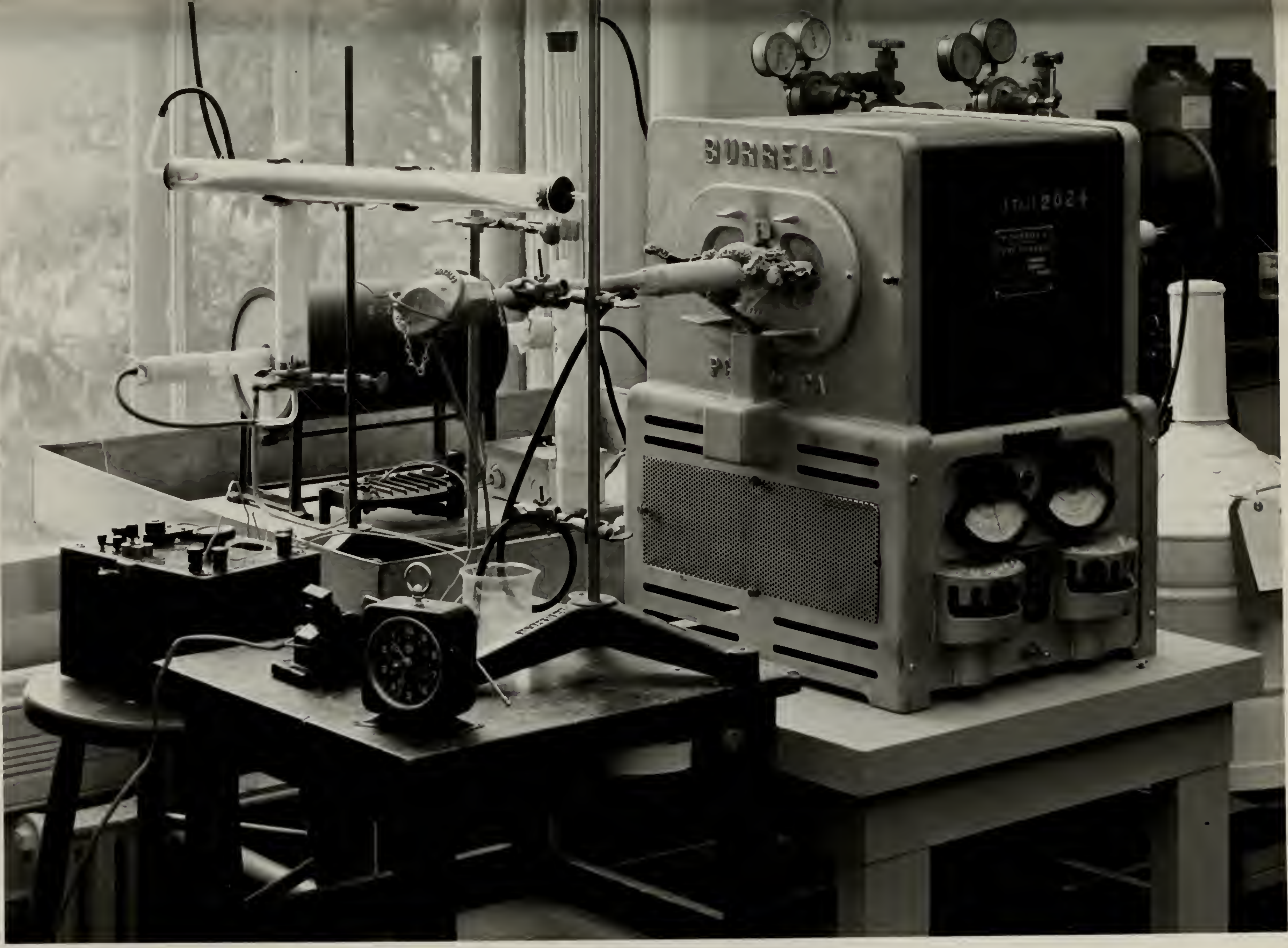


FIGURE 7. General View - Furnace and Purification System (Left)

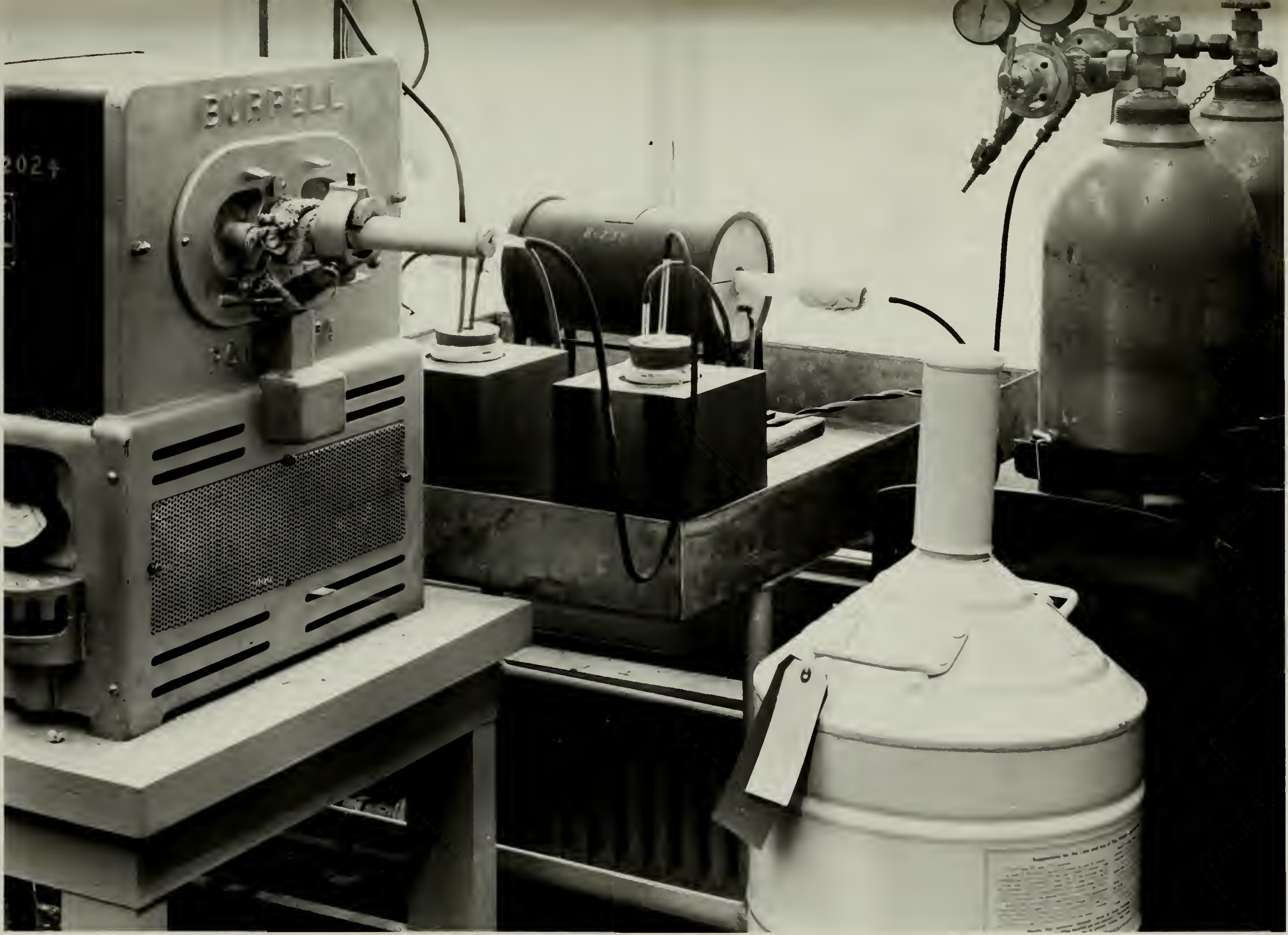


FIGURE [illegible]. General View - Furnace and Purification System (Right)

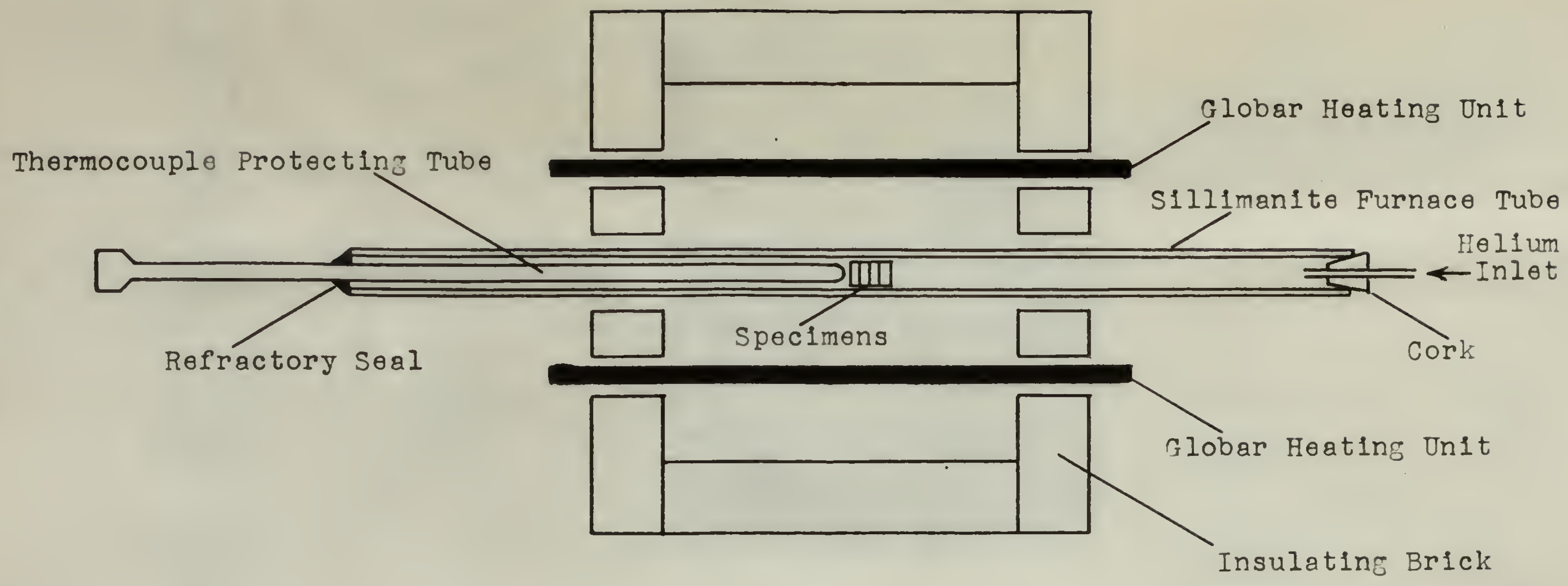


FIGURE 9. Furnace Arrangement - Plan View

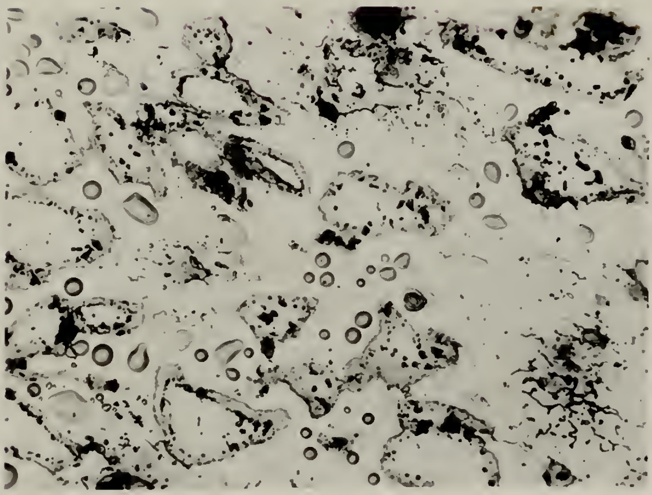


FIGURE 10. X-40 Compacted at 100,000 psi and Sintered For Four Hours at 2100°F. Etched With Chromic Acid and Alkaline Potassium Permanganate (250X)

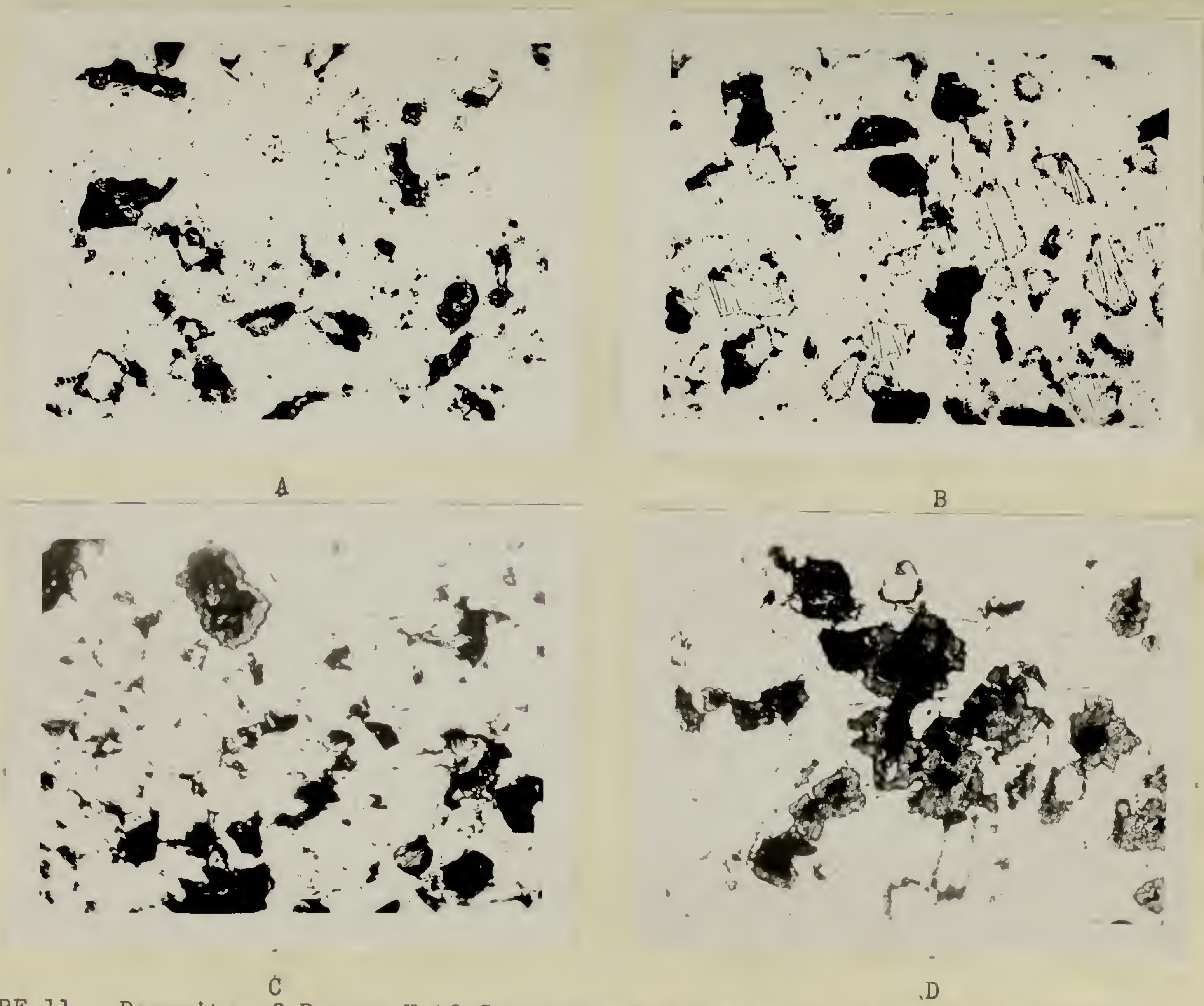


FIGURE 11. Porosity of Porous X-40 Specimens prepared with (a)3.85%, (b)7.42% (C)10.70% and (D)13.80% Ammonium Bicarbonate (100X)

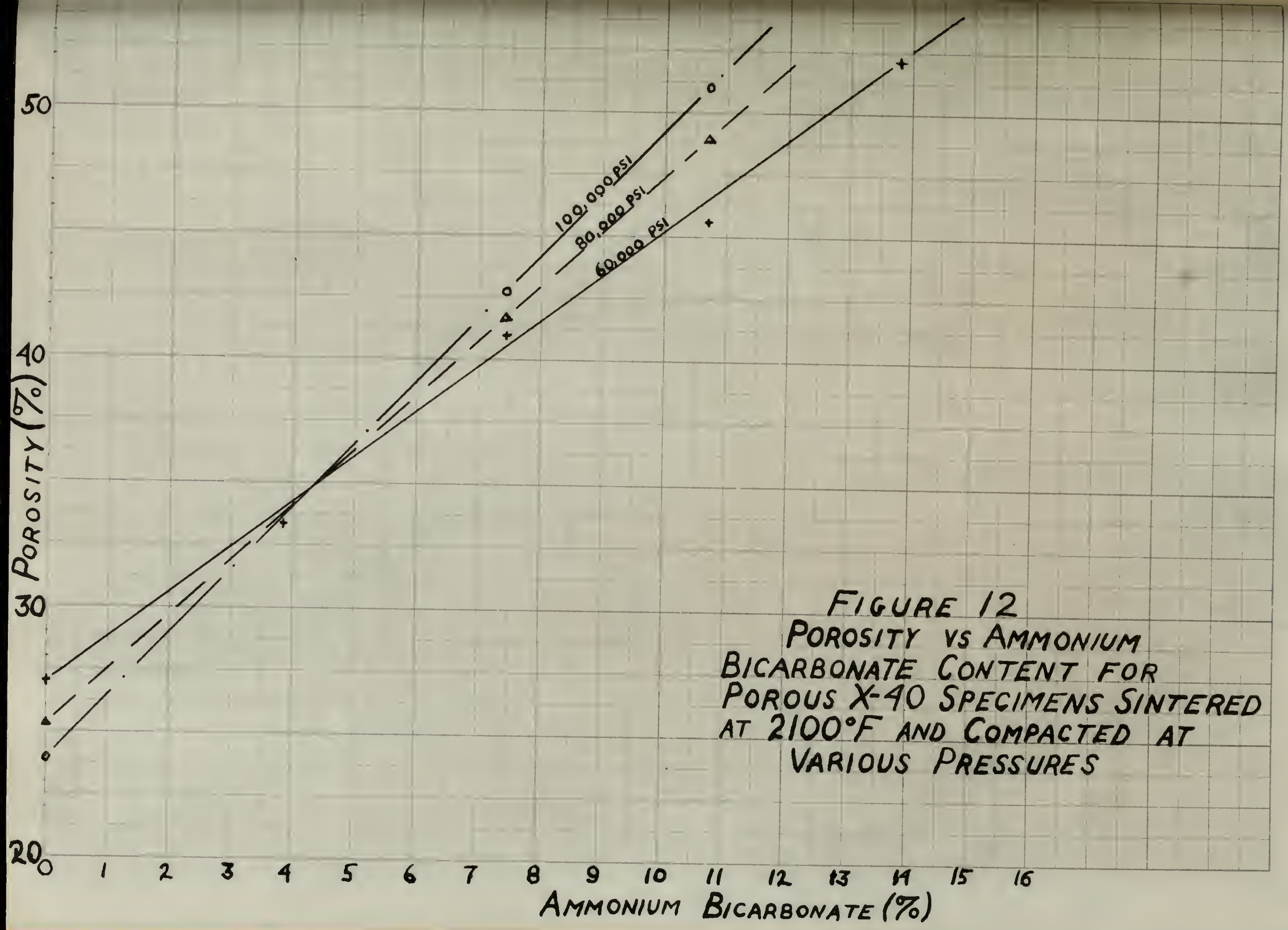


FIGURE 12
POROSITY VS AMMONIUM
BICARBONATE CONTENT FOR
POROUS X-40 SPECIMENS SINTERED
AT 2100°F AND COMPACTED AT
VARIOUS PRESSURES

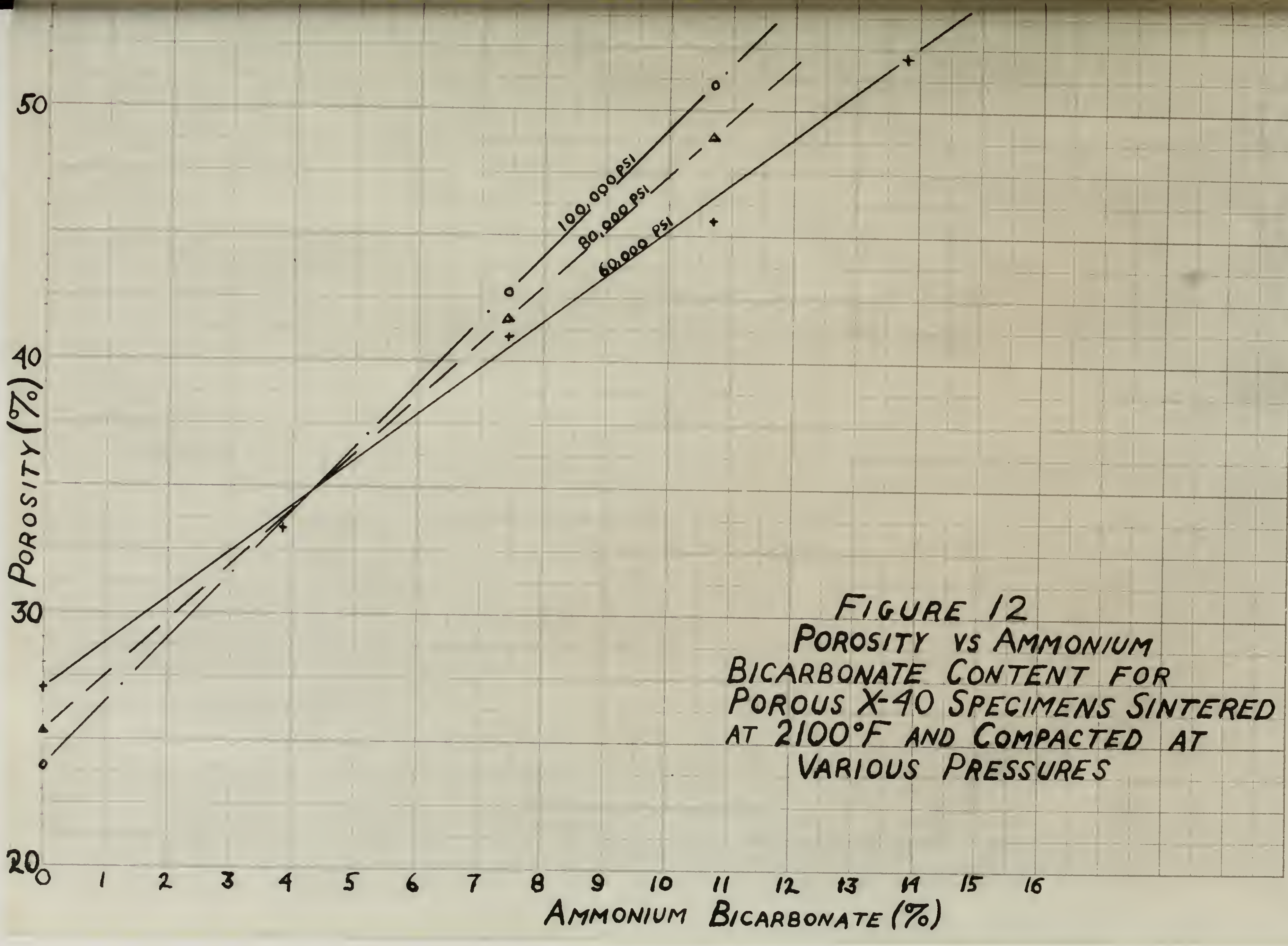


FIGURE 12
POROSITY VS AMMONIUM
BICARBONATE CONTENT FOR
POROUS X-40 SPECIMENS SINTERED
AT 2100°F AND COMPACTED AT
VARIOUS PRESSURES

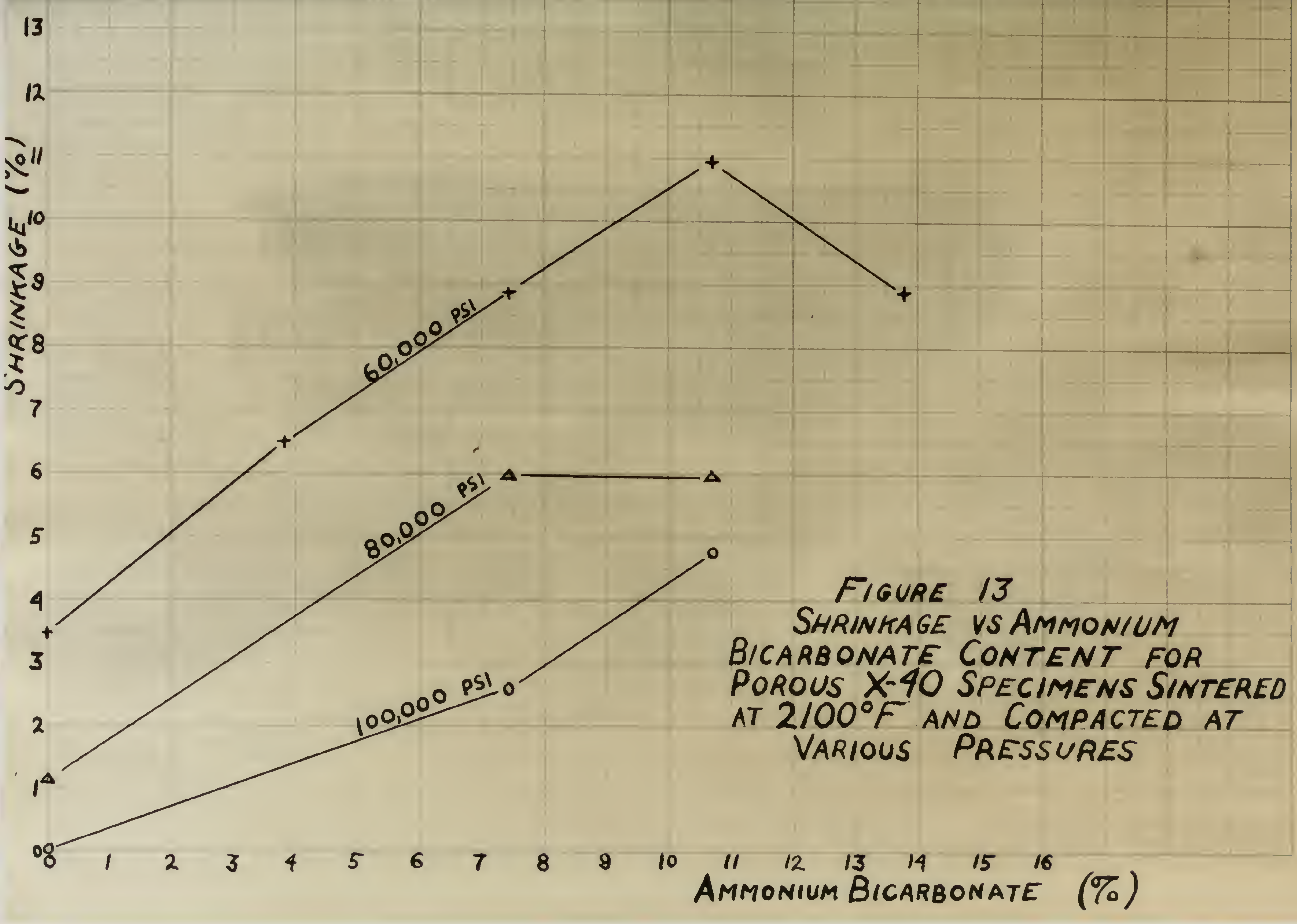


FIGURE 13
SHRINKAGE VS AMMONIUM
BICARBONATE CONTENT FOR
POROUS X-40 SPECIMENS SINTERED
AT 2100°F AND COMPACTED AT
VARIOUS PRESSURES

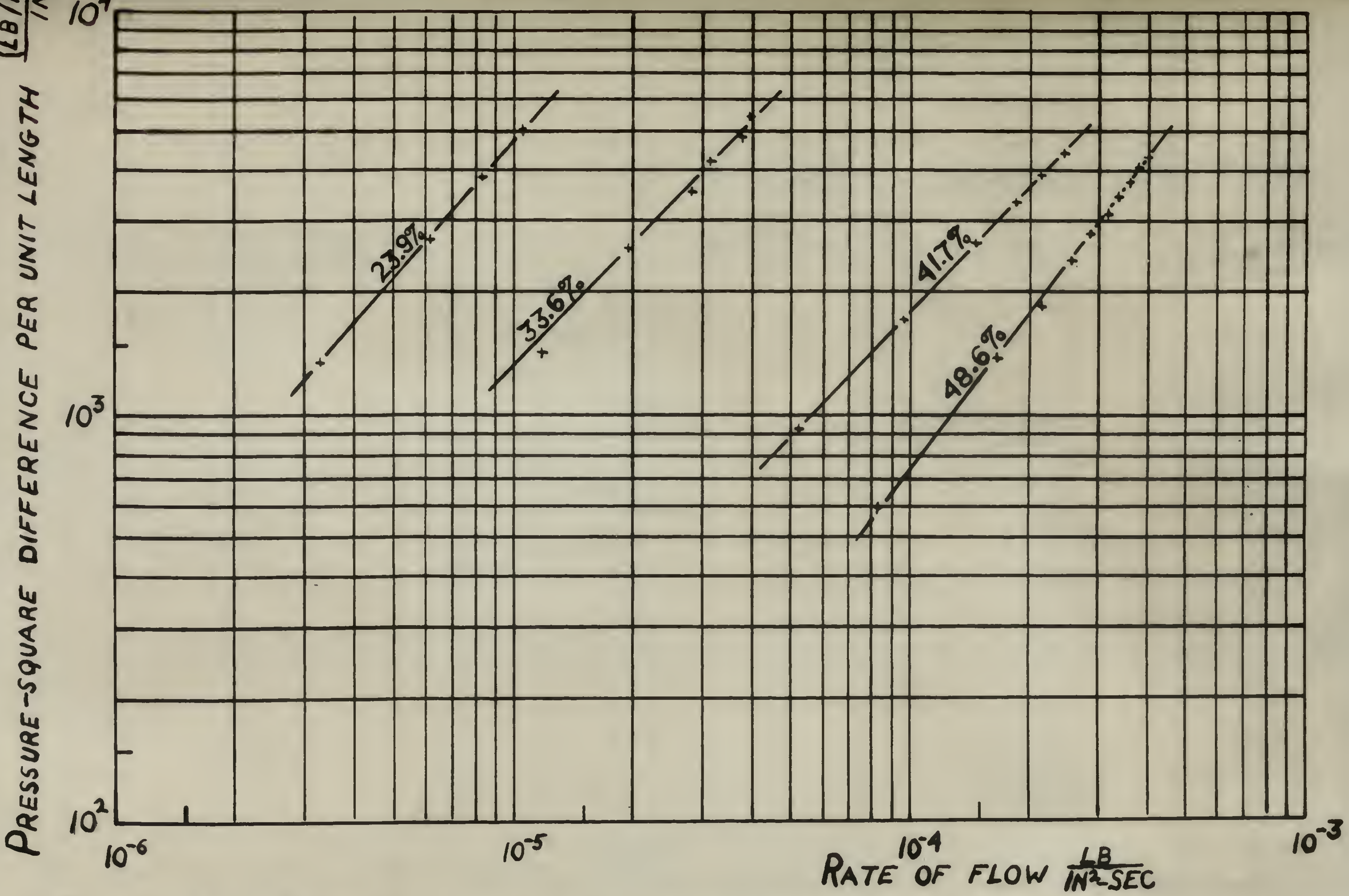


FIGURE 14 PRESSURE-SQUARE DIFFERENCE VS. COMPRESSED AIR RATE OF FLOW FOR VARIOUS POROSITIES.

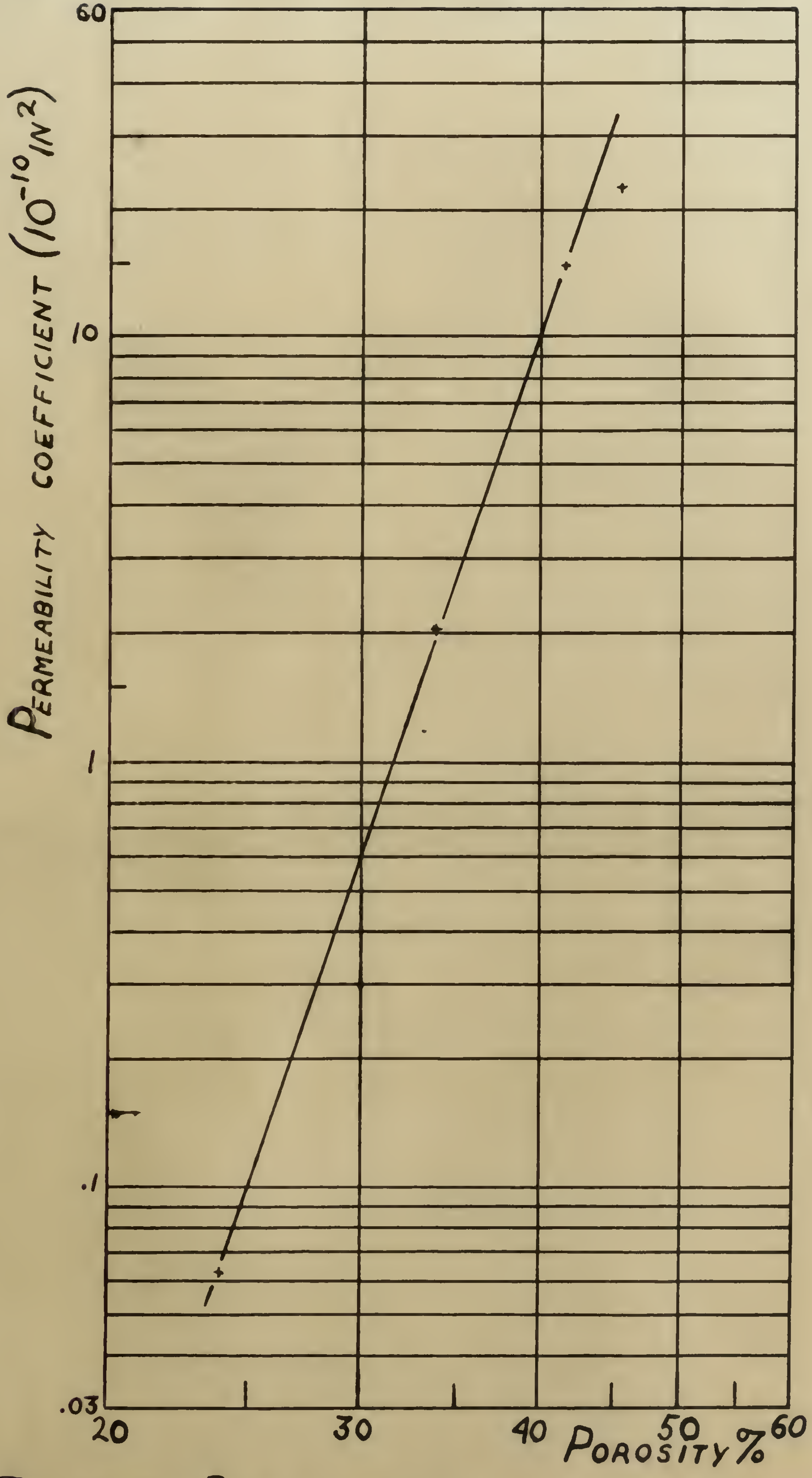


Figure 15 Permeability coefficient vs. Porosity

JUL 2 BINDERY
FEB 16 cor. BINDERY
[illegible] 12 998
NOV 23 RESERVE
NOV 24 DISPLAY

Thesis Glendinning 20652
G458 The preparation of a supe
alloy with controlled porosity.

BINDERY
FEB 16 cor. BINDERY
[illegible] [illegible]
NOV 23 RESERVE
NOV 23 RESERVE
[illegible] DISPLAY

Thesis Glendinning 20652
G458 The preparation of a superalloy
with controlled porosity.

Library
U. S. Naval Postgraduate School
Monterey, California

ARTISAN
GOLD LETTERING
AND
SMITH BINDERY
OAKLAND, CALIF.

thesG458
The preparation of a superalloy with con
3 2768 002 02935 7
DUDLEY KNOX LIBRARY